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# Patterns of the Relationship between the Limit Potentials of the 06KhN28MDT Alloy and Its Indicators in a Gap with a Chloride-Containing Medium Present in the Operation of Heat Exchangers

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The article develops mathematical models based on regression trees to study the relationship between the repassivation potential ($E_{rep}$), free corrosion potential ($E_{cor}$) of the 06KhN28MDT alloy in a chloride-containing media, its chemical composition, and structure. As established, $E_{rep}$ shifts in the positive side with an increase in Cr and Cu contents. Specifically, $E_{rep}$ shifts by 192.4 mV within the Cr content range of 23.12–23.68 wt.% and reaches 0.5 V with Cu content up to 2.73 wt.% and Cr content up to 23.125 wt.%. A reduction in the mean austenite grain diameter from 16.5 to 11 μm shifts $E_{rep}$ to the most negative side of 0.287 V. Additionally, when the Cu content exceeds 2.73 wt.% and Cr exceeds 23.125 wt.%, $E_{rep}$ shifts further by 0.265 and 0.23 V, respectively. The hypothesis suggests that Cr forms dense oxide films, while Cu provides anodic protection to grain boundaries. The $E_{cor}$ potential of the alloy shifts to the most negative side of –0.4557 V as the Cr content decreases from 22.215 down to 21.84 wt.% and Mn decreases from 0.455 down

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to 0.31 wt.%. With carbon content below 0.053 wt.%, $E_{cor}$ is of –0.41 V, while the precipitation of Cr and Mo carbides from the austenite solid solution causes only a slight shift in the negative direction. The most positive $E_{cor}$ value (–0.38 V) is achieved, when the mean austenite grain diameter exceeds 15.5 μm. An increase in Ni content from 27.675 up to 27.730 wt.% shifts $E_{cor}$ in the negative side by 0.17 V, indicating that Ni has a stronger effect on $E_{cor}$ compared to Cr and Cu. As found, a decrease in Cr, Mn, and Ni contents in the alloy accelerates general corrosion, but slows down crevice corrosion due to the redistribution of anodic currents. This trend is caused by the redistribution of anodic currents among a large number of dissolution centres of metal atoms in the alloy composition. The constructed mathematical models are recommended for enterprises, which produce plate-like heat exchangers from this alloy to use to select optimal melts in terms of chemical composition and structure, which will ensure maximum resistance of heat exchanger plates to crevice corrosion in the recycled waters of enterprises.

**Key words:** 06KhN28MDT alloy, crevice corrosion, resistance to crevice corrosion, repassivation potential, free corrosion potential.

У статті розроблено математичні моделі на основі дерев реґресій для дослідження взаємозв'язку між потенціялами репасивації ($E_{rep}$), вільної корозії ($E_{cor}$) стопу 06ХН28МДТ у хлоридовмісному середовищі, його хемічним складом і структурою. Встановлено, що $E_{rep}$ зсувається в позитивний бік зі збільшенням вмісту Cr і Cu. Зокрема, $E_{rep}$ зміщується на 192,4 мВ у діяпазоні вмісту Cr від 23,12 до 23,68 мас.% і сягає 0,5 В за наявности Cu до 2,73 мас.% і Cr до 23,125 мас.%. Зменшення середнього діяметра зерна аустеніту від 16,5 до 11 мкм зміщує $E_{rep}$ до найвід'ємнішого значення у 0,287 В. Водночас, за вмісту Cu > 2,73 мас.% і Cr > 23,125 мас.% $E_{rep}$ зсувається ще на 0,265 В і 0,23 В відповідно. Гіпотеза пояснює, що Cr формує щільні оксидні плівки, а Cu анодно захищає межі зерен. Потенціял $E_{cor}$ стопу зсувається до максимально від'ємного значення у –0,4557 В зі зменшенням вмісту Cr від 22,215 до 21,84 мас.% і Mn від 0,455 до 0,31 мас.%. За вмісту C менше 0,053 мас.% $E_{cor}$ становить –0,41 В, а випадіння карбідів Cr і Mo лише незначно зміщує його у від'ємний бік. Найпозитивніше значення $E_{cor}$ (–0,38 В) досягається за середнього діяметра зерна аустеніту понад 15,5 мкм. Збільшення вмісту Ni від 27,675 до 27,730 мас.% зсуває $E_{cor}$ у від'ємний бік на 0,17 В, що свідчить про сильніший вплив Ni на $E_{cor}$ порівняно з Cr і Cu. З'ясовано, що зменшення вмісту Cr, Mn та Ni у стопі пришвидшує загальну, але уповільнює щілинну корозію через перерозподіл анодних струмів. Таку тенденцію зумовлено перерозподілом анодних струмів між великою кількістю центрів розчинення атомів металів у складі стопу. Побудовані математичні моделі рекомендовано підприємствам, які виробляють пластинчасті теплообмінники з цього стопу, застосовувати для вибору оптимальних топлень за хемічним складом і структурою, які забезпечать максимальний опір пластин теплообмінників щілинній корозії в оборотніх водах підприємств.

**Ключові слова:** стоп 06ХН28МДТ, щілинна корозія, опір щілинній корозії, потенціял репасивації, потенціял вільної корозії.

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## 1. INTRODUCTION

The design features of plate-like heat exchangers can contribute to crevice corrosion during their operation in the circulating systems of enterprises [1, 2]. In particular, work [2] recorded localized corrosion damage at the tops of corrugations between adjacent heat transfer plates, on their surfaces under the recycled water sediment, and at the ends of the groove for the rubber gasket. It is known [3, 4] that, under such conditions, chloride-containing media can be acidified due to the hydrolysis of corrosion products, accumulate chlorides, and locally increase the temperature. The authors of studies [5–9] found that the parameters of model-recycled waters, characterized by pH and chloride concentration, have the most intense effect on the pitting resistance of AISI 304 [5, 6], AISI 321 [7, 8] steels, and 06KhN28MDT alloy [9]. The effect of their structural heterogeneity on critical pitting temperatures is half that of the media parameters, but higher than the chromium content. Taking into account such dependences, some scientists [10–14] propose protective coatings on the surface of heat transfer elements of heat exchangers to prevent their pitting and crevice corrosion in the recycled waters of enterprises. In particular, coatings based on composite [10, 11], polymeric [12, 13], and nanostructured films [14] are considered promising today, as they reliably prevent the contact of passivated steels and alloys with chloride-containing media. This approach provides reliable protection of steels and alloys against local corrosion, but it is quite expensive and time-consuming. At the same time, papers [5–9] used a different approach to prevent such problems; in particular, they developed mathematical models that establish the relationship between the CPT of steels and alloys and their chemical composition, structure components, and parameters of model-recycled waters. This approach does not require additional resources, and therefore is promising. Therefore, the article establishes the dependence between the limit potentials of the 06KhN28MDT alloy and its indicators in a gap with a chloride-containing medium present during the operation of plate-like heat exchangers.

## 2. EXPERIMENTAL/THEORETICAL DETAILS

In this paper, five industrial melts of 06KhN28MDT alloy (analogous to AISI 904L steel), which is used for the production of heat exchangers, have been studied.

The chemical composition of the alloy has been previously determined [15] by chemical analytical and XRD methods using the SRM-25 installation. It is given in Table 1. In this Table: $x_1$—C, carbon content in steel, wt.% ($\leq 0.06$); $x_2$—Mn, manganese content in steel, wt.%

**TABLE 1.** A real sample of dependences based on the results of the sample studies.

| Nos. alloy melts | $x_1$ | $x_2$ | $x_3$ | $x_4$ | $x_5$ | $x_6$ | $x_7$ | $x_8$ | $x_9$ | $x_{10}$ | $x_{11}$ | $E_{cor}$, V | $E_{rep}$, V | $\Delta E$, V |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.05 | 0.32 | 0.6 | 24.31 | 27.39 | 0.79 | 2.9 | 2.75 | 0.1711 | 0.0091 | 11 | –0.4 | 0.8 | 1.2 |
| 2 | 0.067 | 0.46 | 0.57 | 22.68 | 27.65 | 0.59 | 2.78 | 2.68 | 0.1427 | 0.0036 | 24 | –0.43 | 0.5 | 0.93 |
| 3 | 0.068 | 0.54 | 0.55 | 21.84 | 27.45 | 0.55 | 2.55 | 2.6 | 0.1918 | 0.0043 | 29 | –0.42 | 0.22 | 0.64 |
| 4 | 0.048 | 0.57 | 0.62 | 22.67 | 27.73 | 0.67 | 2.56 | 2.53 | 0.1692 | 0.0043 | 31 | –0.4 | 0.55 | 0.95 |
| 5 | 0.05 | 0.31 | 0.57 | 23.46 | 27.51 | 0.89 | 2.51 | 2.78 | 0.0931 | 0.0036 | 15 | –0.38 | 0.6 | 0.98 |
| min | 0.048 | 0.31 | 0.55 | 21.84 | 27.39 | 0.55 | 2.51 | 2.53 | 0.0931 | 0.0036 | 11 | –0.5 | 0.1 | |
| max | 0.068 | 0.57 | 0.62 | 24.31 | 27.73 | 0.89 | 2.9 | 2.78 | 0.1918 | 0,0091 | 29 | –0.1 | 0.7 | |
| multiplicity | 0.001 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.0001 | 0,0001 | 1 | 0.01 | 0.01 | 0.01 |

(< 0.8); $x_3$—Si, silicon content in steel, wt.% (< 0.8); $x_4$—Cr, chromium content in steel, wt.% (22.00–25.00); $x_5$—Ni, nickel content in steel, wt.% (26.00–29.00); $x_6$—Ti, titanium content in steel, wt.% (0.5–0.9); $x_7$—Mo, molybdenum content in steel, wt.% (2.5–3.0); $x_8$—Cu, copper content in steel, wt.% (2.5–3.5); $x_9$—volume of titanium carbonitrides, vol.% (0.0931–0.1918); $x_{10}$—volume of titanium sulphides, vol.% (0.0036–0.0091); $x_{11}$—$d_g$, mean austenite grain diameter in the alloy, μm (11–31); $E_{cor}$ is the free corrosion potential, V; $E_{rep}$ is the repassivation potential, V; $\Delta E_{rep}$ is the criterion, V.

The variances of deviation of the alloy components are: carbon ±0.002, silicon ±0.004, manganese ±0.01, chromium ±0.02, nickel ±0.03, molybdenum ±0.02, copper ±0.02, titanium ±0.02, phosphorus ±0.02, sulphur ±0.003 [wt.%]. The components of the structural heterogeneity of the 06HN28MDT alloy have been determined in [15].

The resistance of 06KhN28MDT alloy to crevice corrosion was evaluated by the ultimate repassivation potentials $E_{rep}$, free corrosion $E_{cor}$, and $\Delta E_{rep}$ by the criterion determined by the formula

$$\Delta E_{rep} = E_{rep} - E_{cor}. \quad (1)$$

The alloy was considered to be resistant to crevice corrosion, if $\Delta E > 0.05$ V [16]. The real values of the limit potentials $E_{rep}$, $E_{cor}$, and $\Delta E$ of the 06KhN28MDT alloy criterion are given in Table 1. The generated variable factors ($x_1$, ..., $x_{11}$) and output factors $E_{cor}$, $E_{rep}$, and $\Delta E_{rep}$ are shown in Table 2.

Regression trees were used as the basis for constructing mathematical models (Tables 3, 4), which are the most popular method for solving many practical problems [17], since they automatically select informative features (the most important $x_i$ of the model).

The quality of the mathematical models of Tables 3, 4 was evaluated using the sum of squares of instantaneous mistakes [17]:

**TABLE 2.** Generated samples.

| $S$ | $x_1$ | $x_2$ | $x_3$ | $x_4$ | $x_5$ | $x_6$ | $x_7$ | $x_8$ | $x_9$ | $x_{10}$ | $x_{11}$ | $E_{cor}$, V | $E_{rep}$, V |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.05 | 0.32 | 0.60 | 24.31 | 27.39 | 0.79 | 2.90 | 2.75 | 0.1711 | 0.0091 | 11.00 | –0.40 | 0.80 |
| 2 | 0.067 | 0.46 | 0.57 | 22.68 | 27.65 | 0.59 | 2.78 | 2.68 | 0.1427 | 0.0036 | 24.00 | –0.43 | 0.50 |
| 3 | 0.068 | 0.54 | 0.55 | 21.84 | 27.45 | 0.55 | 2.55 | 2.60 | 0.1918 | 0.0043 | 29.00 | –0.42 | 0.22 |
| 4 | 0.048 | 0.57 | 0.62 | 22.67 | 27.73 | 0.67 | 2.56 | 2.53 | 0.1692 | 0.0043 | 31.00 | –0.40 | 0.55 |
| 5 | 0.05 | 0.31 | 0.57 | 23.46 | 27.51 | 0.89 | 2.51 | 2.78 | 0.0931 | 0.0036 | 15.00 | –0.38 | 0.60 |
| 6 | 0.057 | 0.31 | 0.59 | 23.33 | 27.61 | 0.67 | 2.70 | 2.71 | 0.1807 | 0.0039 | 13.00 | –0.41 | 0.33 |
| 7 | 0.061 | 0.51 | 0.62 | 22.15 | 27.51 | 0.78 | 2.66 | 2.75 | 0.1219 | 0.0043 | 23.00 | –0.43 | 0.32 |
| 8 | 0.052 | 0.54 | 0.60 | 22.88 | 27.39 | 0.60 | 2.62 | 2.75 | 0.1524 | 0.0054 | 16.00 | –0.41 | 0.36 |
| 9 | 0.057 | 0.54 | 0.61 | 23.09 | 27.60 | 0.79 | 2.52 | 2.67 | 0.0977 | 0.0059 | 19.00 | –0.39 | 0.54 |
| 10 | 0.048 | 0.33 | 0.61 | 23.16 | 27.51 | 0.67 | 2.57 | 2.57 | 0.1277 | 0.0054 | 25.00 | –0.38 | 0.73 |
| 40 | 0.055 | 0.43 | 0.58 | 23.52 | 27.58 | 0.77 | 2.70 | 2.63 | 0.1402 | 0.0040 | 18.00 | –0.40 | 0.65 |
| 41 | 0.067 | 0.51 | 0.60 | 23.73 | 27.65 | 0.84 | 2.81 | 2.77 | 0.1041 | 0.0058 | 20.00 | –0.40 | 0.87 |
| 42 | 0.053 | 0.32 | 0.60 | 23.63 | 27.44 | 0.60 | 2.78 | 2.63 | 0.1006 | 0.0059 | 14.00 | –0.40 | 0.73 |
| 43 | 0.064 | 0.55 | 0.55 | 23.45 | 27.62 | 0.64 | 2.84 | 2.60 | 0.0958 | 0.0041 | 25.00 | –0.41 | 0.95 |
| 44 | 0.062 | 0.51 | 0.59 | 23.88 | 27.40 | 0.69 | 2.61 | 2.65 | 0.1800 | 0.0051 | 22.00 | –0.37 | 0.85 |
| 45 | 0.049 | 0.35 | 0.61 | 22.32 | 27.67 | 0.66 | 2.77 | 2.54 | 0.1656 | 0.0063 | 28.00 | –0.44 | 0.42 |
| 46 | 0.054 | 0.41 | 0.56 | 24.22 | 27.54 | 0.5800 | 2.79 | 2.66 | 0.1255 | 0.0077 | 26.00 | –0.37 | 1.22 |
| 47 | 0.053 | 0.45 | 0.58 | 22.23 | 27.59 | 0.87 | 2.55 | 2.75 | 0.1474 | 0.0060 | 14.00 | –0.43 | 0.03 |
| 48 | 0.053 | 0.43 | 0.59 | 22.72 | 27.65 | 0.85 | 2.80 | 2.63 | 0.1527 | 0.0071 | 13.00 | –0.45 | 0.18 |
| 49 | 0.058 | 0.39 | 0.59 | 24.17 | 27.54 | 0.56 | 2.87 | 2.76 | 0.1285 | 0.0050 | 25.00 | –0.39 | 1.19 |
| 50 | 0.058 | 0.46 | 0.60 | 22.07 | 27.69 | 0.87 | 2.55 | 2.74 | 0.1829 | 0.0037 | 20.00 | –0.43 | –0.02 |

$$E = \sum_{S=1}^{S} (y^S - y^{S*})^2 . \quad (2)$$

The sum of the squared mistakes for the potential: $E_{cor} = 0.0027$ V, $E_{rep} = 0.2894$ V; the standard deviation: $E_{cor} = 0.0001$ V, $E_{rep} = 0.0058$ V.

## 3. RESULTS AND DISCUSSION

According to the results of the analysis of the constructed mathematical model (Table 2), which is based on the defined regression trees (Fig. 1), the following trend was established, in particular, if the parameter of the 06KhN28MDT alloy $x_4$(Cr) < 23.055 wt.%, then, we move to node 2, where, if $x_2$(Mn) < 0.455 wt.%, then we move to node 4, then, provided that $x_4$(Cr) < 22.215 wt.%, the free corrosion potential of the alloy $E_{cor}$ is of –0.455714 V (node 3). It turns out that the most negative value of the potential $E_{cor}$ of the alloy in the gap correlates with a low content of chromium and manganese within the standard for its production (Table 1). It should be noted that under such conditions, the resistance of the studied alloy to crevice corrosion in the model chlo-

**TABLE 3.** Mathematical model that establishes the relationship between the corrosion potential $E_{cor}$ of 06KhN28MDT alloy and its chemical composition and structure components, based on regression trees.

| Item No. | Dependences |
|---|---|
| 1 | if $x_4 < 23.055$ then node 2 else; if $x_4 >= 23.055$ then node 3 else –0.4126 |
| 2 | if $x_4 < 23.055$ then node 2 else; if $x_4 >= 23.055$ then node 3 else –0.4126 |
| 3 | if $x_5 < 27.575$ then node 6 else; if $x_5 >= 27.575$ then node 7 else –0.38875 |
| 4 | if $x_4 < 22.215$ then node 8 else; if $x_4 >= 22.215$ then node 9 else –0.444 |
| 5 | if $x_1 < 0.053$ then node 10 else; if $x_1 >= 0.053$ then node 11 else –0.421818 |
| 6 | if $x_{11} < 14.5$ then node 12 else; if $x_{11} >= 14.5$ then node 13 else –0.379286 |
| 7 | if $x_5 < 27.675$ then node 14 else; if $x_5 >= 27.675$ then node 15 else –0.402 |
| 8 | fit = –0.455714 |
| 9 | fit = –0.43375 |
| 10 | fit = –0.41 |
| 11 | fit = –0.42625 |
| 12 | fit = –0.4 |
| 13 | if $x_8 < 2.755$ then node 16 else; if $x_8 >= 2.755$ then node 17 else –0.375833 |
| 14 | fit = –0.3975 |
| 15 | fit = –0.42 |
| 16 | fit = –0.37125 |
| 17 | fit = –0.385 |

ride-containing media increases as its $\Delta E$ criterion, which was determined by Eq. (1), increases [16]. This is due to the fact that the lower the potential $E_{cor}$ of the alloy, the easier it is to give up electrons, contributing to the ionization of metals in its composition at the anode sites. Under such conditions, the density of anode currents in them decreases due to their redistribution among a larger number of anode sites. This is consistent with the information presented in Refs. [18, 19]. This tendency 'slows down' the transformation of metastable local corrosion damage into stable damage.

A decrease in the content of manganese, as a surface-active chemical element, most likely contributes to the depletion of the oxide film on the surface of the 06HN28MDT alloy by chromium, which leads to a shift its potential $E_{cor}$ to the negative side. Our hypothesis is based on the information that Mn and Cu contribute to the formation of a passive film enriched in chromium [20].

From the analysis of the mathematical model (Table 3), it follows that, if the chromium content in the alloy under study $x_4(\mathrm{Cr}) \geq 23.055$ V, then, its potential $E_{cor}$ shifts to a positive side to –0.4126 V (item 1, Table 3). However, provided that $x_5(\mathrm{Ni}) < 27.57$ wt.% (item 3, Table 3), and $x_{11}[d_g] < 14.5$ μm (item 6, Table 3), its potential $E_{cor}$ is of –0.4 V (item 12, Table 3). These dependences between the potential $E_{cor}$ of

**TABLE 4.** Mathematical model that establishes the relationship between the repassivation potential $E_{rep}$ of 06KhN28MDT alloy and its chemical composition and structure components based on regression trees.

| Item No. | Dependences |
|---|---|
| 1 | if $x_4 < 23.43$ then node 2 else; if $x_4 >= 23.43$ then node 3 else 0.5538 |
| 2 | if $x_4 < 22.315$ then node 4 else; if $x_4 >= 22.315$ then node 5 else 0.336774 |
| 3 | if $x_{11} < 22.5$ then node 6 else; if $x_{11} >= 22.5$ then node 7 else 0.907895 |
| 4 | if $x_{11} < 22$ then node 8 else; if $x_{11} >= 22$ then node 9 else 0.150769 |
| 5 | if $x_{11} < 16.5$ then node 10 else; if $x_{11} >= 16.5$ then node 11 else 0.471111 |
| 6 | if $x_4 < 23.68$ then node 12 else; if $x_4 >= 23.68$ then node 13 else 0.786364 |
| 7 | fit = 1.075 |
| 8 | fit = 0.07875 |
| 9 | fit = 0.266 |
| 10 | fit = 0.286667 |
| 11 | if $x_8 < 2.73$ then node 14 else; if $x_8 >= 2.73$ then node 15 else 0.563333 |
| 12 | fit = 0.6725 |
| 13 | fit = 0.851429 |
| 14 | if $x_4 < 23.125$ then node 16 else; if $x_4 >= 23.125$ then node 17 else 0.523 |
| 15 | fit = 0.765 |
| 16 | fit = 0.5 |
| 17 | fit = 0.73 |

06KhN28MDT alloy in a gap with a model chloride-containing medium and the content of nickel in it and the size of the austenite grain show that the smaller they are, the more positive it is. Under such conditions, the ionization of metals in its composition that are in contact with the medium becomes more difficult. At the same time, it should be noted that the finer the grain of the alloy austenite, the lower the degree of incoherence between adjacent crystal-lattice atoms, and the higher the resistance of metal atoms located at the grain boundaries to ionization when in contact with a chloride-containing medium. This helps to increase the potential $E_{cor}$ of the alloy and reduce its resistance to crevice corrosion in a chloride-containing media.

The influence of nickel on the resistance of 06HN28MDT alloy to crevice corrosion in a chloride-containing media cannot be assessed only by the above dependences ($E_{cor}$–Ni content). After all, in Ref. [21], it was found that steel consisting of 21 wt.% Cr, 6 wt.% Ni, and 2 wt.% Mo has high pitting resistance in chloride-containing media because of its pitting potential $E_{pit}$ is of 0.56 V. However, in 0Kh21N5T steel, it is equal to 0.428 V, which is due to the absence of molybdenum and a decrease in nickel content by 0.7 wt.%.

A further decrease in nickel content to 3.2 wt.% accelerates the shift of the potential to the negative side. In addition, the role of nickel in

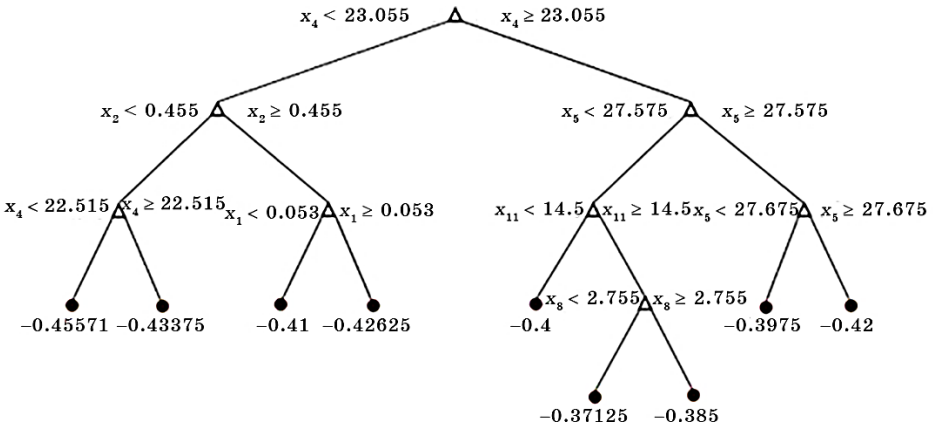



**Fig. 1.** Regression tree showing the relationship between the free corrosion potential $E_{cor}$ of 06KhN28MDT alloy in a gap with a chloride-containing solution and its chemical composition and structural components.

the pitting resistance of stainless steels is evidenced by the higher value of the potential $E_{pit}$ (0.23V) of Kh14Mn14N3T steel at its content of 3.1 wt.%, than Kh17AMn14 with higher chromium content. At the same time, it should be noted that the pitting resistance of the stainless steel 12Kh18N10T in chloride-containing media is much higher than that of these steels. This information shows that a decrease in the chromium content in steels reduces their pitting resistance more intensively than that of nickel, even in the presence of a two-phase structure [21, 22].

It should be noted that the mechanisms of pitting and crevice corrosion of stainless steels and alloys in chloride-containing media are very similar, so, the effect of nickel on their limit potentials is likely to be the same. Obviously, it is not associated with compensating for the negative effect of MnS inclusions on the pitting resistance of the alloy, as is believed in Refs. [23, 24] for the chromium-nickel-molybdenum steel 13Kh17N11M3, since only carbonitrides (Fig. 2) and titanium sulphides (Fig. 3), which are even insoluble in solutions of many acids, have been recorded in the 06KhN28MDT alloy [25]. However, the potential $E_{cor}$ of the 06KhN28MDT alloy depends on the chromium content in the alloy and its grain size.

After all, from the analysis of items 1, 3, 6, 12 of the mathematical model (Table 3), it was found that the potential $E_{cor}$ of the 06KhN28MDT alloy shifts by 0.0126 V in the positive direction if the chromium content in it is more than 23.055 wt.%, nickel less than 27.575 wt.%, provided that the mean austenite grain diameter is less than 14.5 μm. It was found that the potential $E_{cor}$ of the studied alloy shifts to the negative side to –0.434615 V with an increase in the man-

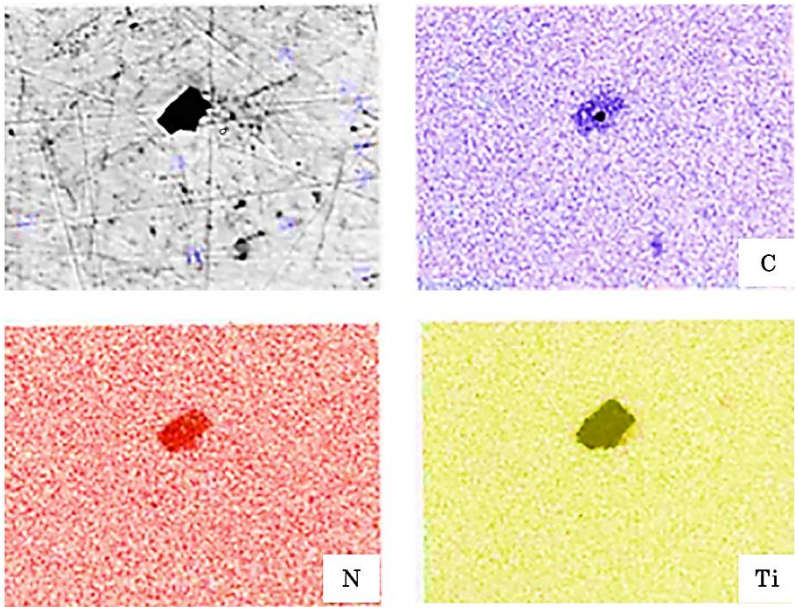



**Fig. 2.** Titanium carbonitrides in alloy 06HN28MDT (×550).

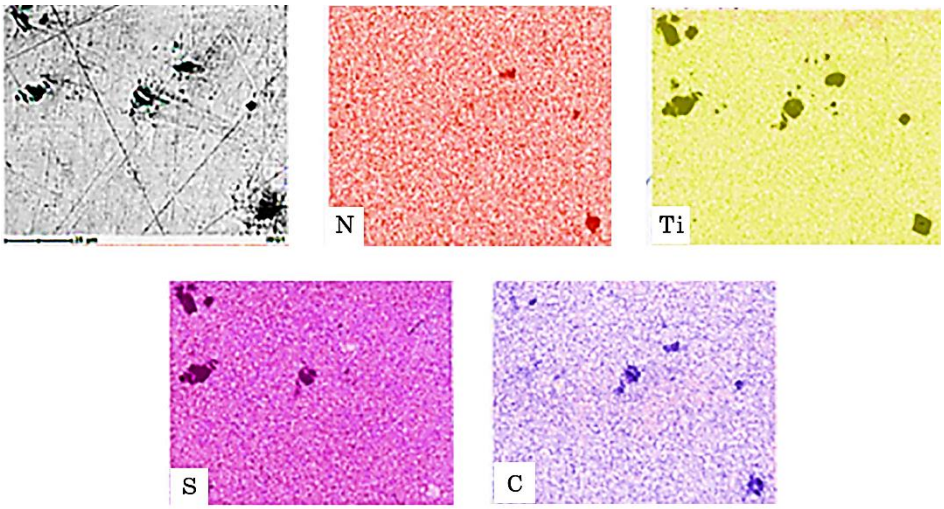



**Fig. 3.** Titanium sulphides and carbonitrides in 06HN28MDT alloy (×550).

ganese content from 0.455 up to 0.57 wt.% (item 2 of Table 3).

However, under the same conditions, when the carbon content ($x_1$)) less than 0.053 wt.%, its potential $E_{cor}$ is of –0.41 V (items 5, 10 of Table 3). Thus, it can be noted that the potential $E_{cor}$ of the alloy under

study shifts to the positive side by 0.0246 V (see items 1, 10 of Table 3), which reduces the rate of general corrosion but increases the probability of crevice corrosion. The mechanisms of this process were mentioned above. In addition, at such carbon content in the alloy, according to Ref. [25], it is almost completely dissolved in the austenite solid solution. Under such conditions, the length of the boundaries of inclusions with the austenitic matrix decreases due to a decrease in the volume of the carbide phase in the vicinity of titanium nitrides and a decrease in the total length of the boundaries of austenite grains and inclusions with its solid solution.

From the analysis of the mathematical model (item 3 of Table 3), it was found that if the nickel content ($x_5$) in the alloy is greater than or equal to 27.575 wt.%, then, its potential $E_{cor}$ is of –0.38878 V. Consequently, under such conditions, it has practically the most positive value, which contributes to a decrease in $\Delta E$ criterion of the alloy and its resistance to crevice corrosion. This is due to the fact that the critical passivation potential of Ni (+0.15 V) is much more negative than that of Fe (+0.46 V) [26]. However, when the nickel content in the alloy under study is less than 27.675 wt.% (item 7 of Table 3), its potential $E_{cor}$ is of –0.3975 V (item 14 of Table 3). These dependences indicate that the corrosion potential $E_{cor}$ of the 06KhN28MDT alloy is of about –0.39 V, when the nickel content in it varies in the range from 27.575 up to 27.675 wt.%. It has been recorded that chromium contributes to the shift of the potential $E_{cor}$ of the studied alloy in the negative direction to –0.444 V (item 4 of Table 3). However, according to the information (items 4, 9 of Table 3), under some conditions it can have a slightly more positive value ($E_{cor} = -0.43375$ V). Thus, according to the results of data analysis (items 4, 9 of Table 3), it turns out that the corrosion potential $E_{cor}$ of 06KhN28MDT alloy has the most negative value when the chromium content in it is higher than 22.215 wt.%. This is due to the fact that under such conditions, according to Gerasimov [27], the surface of the alloy is covered with a monolayer of chromium atoms. It is known [26] that the critical passivation potential of chromium is even more negative (–0.35 V) than that of molybdenum (–0.20 V) and titanium (–0.25 V). This tendency contributes to the fact that the $\Delta E$ criterion of the 06KhN28MDT alloy increases, since its corrosion potential $E_{cor}$ shifts significantly to the negative side when it contains more than 22.215 wt.% chromium. The mechanisms of increasing the resistance of the studied alloy to crevice corrosion in a chloride-containing media under the condition of a negative shift in the potential $E_{cor}$ were mentioned above.

It was mentioned above (item 2 of Table 3) that the potential $E_{cor}$ of the 06KhN28MDT alloy was –0.434615 V, if the manganese content in it was less than 0.455 wt.%, or –0.41 V, provided that $x_1(\mathrm{C}) < 0.053$ wt.% (items 5, 10 of Table 3). However, with an increase in the carbon

content in the alloy above 0.053 wt.%, a shift of its corrosion potential $E_{cor}$ in the negative direction to –0.421818 V (item 5 of Table 3) or to –0.42625 V (item 11 of Table 3) has been recorded. This tendency is most likely due to the fact that manganese increases the solubility of carbon in the solid solution of austenite of 06KhN28MDT alloy, since there is information that it and chromium [28] thus affect the solubility of nitrogen, which, like carbon, is a chemical element of the introduction in the crystal lattice of a solid solution of austenite of stainless steels and alloys. This contributes to the growth of its parameters and, obviously, facilitates the ionization of chromium atoms on the surface of the 06KhN28MDT alloy. Under such conditions, the released electrons accumulate on its surface, shifting the free corrosion potential $E_{cor}$ to the negative side. This contributes to an increase in the $\Delta E$ criterion of the studied alloy in a crevice with a chloride-containing medium and, taking into account information from [16], increases its resistance to crevice corrosion.

It was mentioned above that the free corrosion potential $E_{cor}$ of the 06KhN28MDT alloy in the gap with a model chloride-containing medium was –0.4 V (see item 12 of Table 3) if its mean austenite grain diameter ($x_{11}$) was less than 11.4 μm (item 6 of Table 3). However, with its growth over 14.5 μm, a shift in the potential $E_{cor}$ of the alloy to the positive side to –0.379286 V has been recorded (item 6 of Table 3). This corrosion behaviour of the studied alloy in a chloride-containing medium is due to the segregation of copper, as a surface-active chemical element, by the boundaries of austenite grains. Indeed, from the analysis of the dependences, it was found that, if $x_{11}[d_g] \geq 14.5$ μm (item 6 of Table 3), then, provided $x_8(\text{Cu}) < 2.755$ wt.% (item 11 of Table 3), the potential $E_{cor}$ of the 06KhN28MDT alloy is of –0.37125 V (item 16 of Table 3). At the same time, if the copper content in the alloy was higher than 2.765 wt.%, it ranged from –0.375833 (item 13 of Table 3) to –0.385 V (item 17 of Table 3). Thus, summarizing this information, it should be noted that the potential $E_{cor}$ of the 06KhN28MDT alloy shifts to the negative side by 9.2 mV with an increase in its copper content from 2.755 up to 2.78 wt.% (melt 2 of Table 1). At the same time, it shifts in the same direction by 20.7 mV with an increase in the mean austenite grain diameter from 14.5 up to 31 μm (item 6 of Table 3). Thus, it can be noted that the effect of the mean austenite grain diameter of the 06KhN28MDT alloy on its potential $E_{cor}$ is more than twice as great as the copper content. However, in general, the higher the copper content in the alloy and its mean austenite grain diameter, the more negative the value of the $E_{cor}$ potential. This positively affects the alloy resistance to crevice corrosion in a chloride-containing media by the above mechanisms.

It was mentioned above about the effect of nickel in the composition of the 06KhN28MDT alloy on its corrosion potential $E_{cor}$ in a gap with a

chloride-containing medium (item 3 of Table 3). In particular, it was found that it is of –0.4 V (item 12 of Table 3), when the nickel content in the alloy is less than 27.575 wt.%, and the mean austenite grain diameter is of 14.5 μm. It should be noted that the potential $E_{cor}$ of the studied alloy shifts to the negative side to –0.379286 V (item 6 of Table 3) with an increase in the mean austenite grain diameter ($x_{11}$) from 14.5 up to 31 μm and to –0.402 V (item 7 of Table 3) or –0.42 V (item 15 of Table 3) with an increase in the nickel content from 27.675 up to 27.75 wt.% (Table 1). Under such conditions, the potential $E_{cor}$ of the 06KhN28MDT alloy shifts in the negative direction by 20.7 mV with an increase in the mean austenite grain diameter by 16.5 μm (items 6, 12 of Table 3) and by 4.5 (item 7 of Table 3) or 22.5 V (item 15 of Table 3) in the positive direction with an increase in its nickel content by 0.055 wt.%. Thus, it turns out that nickel has a much stronger effect on the potential $E_{cor}$ of the 06KhN28MDT alloy in the gap than the mean austenite grain diameter. At the same time, it should be noted that the joint effect of these alloy parameters on its $E_{cor}$ potential is manifested when $x_5$(Ni) < 27.575 wt.% (items 3, 6 of Table 3), since it shifts to the negative side by 20.7 mV with an increase in the mean austenite grain diameter from 14.5 up to 31 μm.

Summarizing the above, it can be noted that the corrosion potential $E_{cor}$ of 06KhN28MDT alloy in a crevice with a chloride-containing solution depends on the content of chromium, manganese, nickel, carbon, copper, and the mean diameter of the austenite grain. In particular, the synergistic effect of chromium and manganese on this potential was revealed, since it has a maximum negative value (–0.455714 V), when the chromium content is less than 22.215 wt.%, and manganese 0.455 wt.%. This contributes to the growth of the $\Delta E$ criterion of the alloy and its resistance to crevice corrosion. At the same time, it was found that the potential $E_{cor}$ of the studied alloy decreases to –0.4126 V when the chromium content in it is greater than 23.055 wt.%. This is due to the difficulty of ionization of metal atoms in the alloy, since its surface consists of a monolayer of chromium atoms that form a dense passive film.

In addition, with such chromium content in the alloy, provided that the nickel content is less than 27.575 wt.% and the mean austenite grain diameter is of 14.5 μm, its potential $E_{cor}$ is further shifted to the positive side to –0.4 V. This leads to a decrease in the $\Delta E$ criterion of the 06KhN28MDT alloy and its resistance to crevice corrosion. This tendency is due to the fact that at the minimum austenite grain diameter in the alloy, the lowest degree of incoherence between the atoms of adjacent crystal lattices is recorded at its boundaries, which complicates the ionization of metal atoms in these areas of the alloy. Meanwhile, the less nickel in the alloy than the above-mentioned amount, the more positive the value of the potential $E_{cor}$, since the lower the

nickel content in it, the more iron, whose critical ionization potential (+0.46 V) is more than three times more positive than that of nickel (+0.15 V). At the same time, it was found that the larger the mean grain diameter of the austenite of the 06KhN28MDT alloy is over 14.5 μm, the more positive the value of its corrosion potential $E_{cor}$. At the same time, it is of 13.8 mV more positive when the copper content in the alloy is less than 2.755 wt.%. This is most likely due to the fact that copper, as a surface-active chemical element, can segregate at the grain boundaries of austenite, which increases the potential gradient between the austenite solid solution and its grain boundaries, promoting the ionization of metal atoms and the accumulation of electrons on the alloy surface.

The analysis (Fig. 4) showed that the repassivation potential $E_{rep}$ of the 06KhN28MDT alloy, which is characterized by its ability to restore protective passive films in local corrosion damage, depends on the content of chromium ($x_4$), copper ($x_8$), and the mean austenite grain diameter ($x_{11}$). It should be noted that, unlike the corrosion potential $E_{cor}$ of the alloy under study, it does not depend on the content of manganese and nickel, which, as established above, significantly affect the ability of metal atoms in its composition to ionize.

From the analysis of the mathematical model (Table 4), it follows

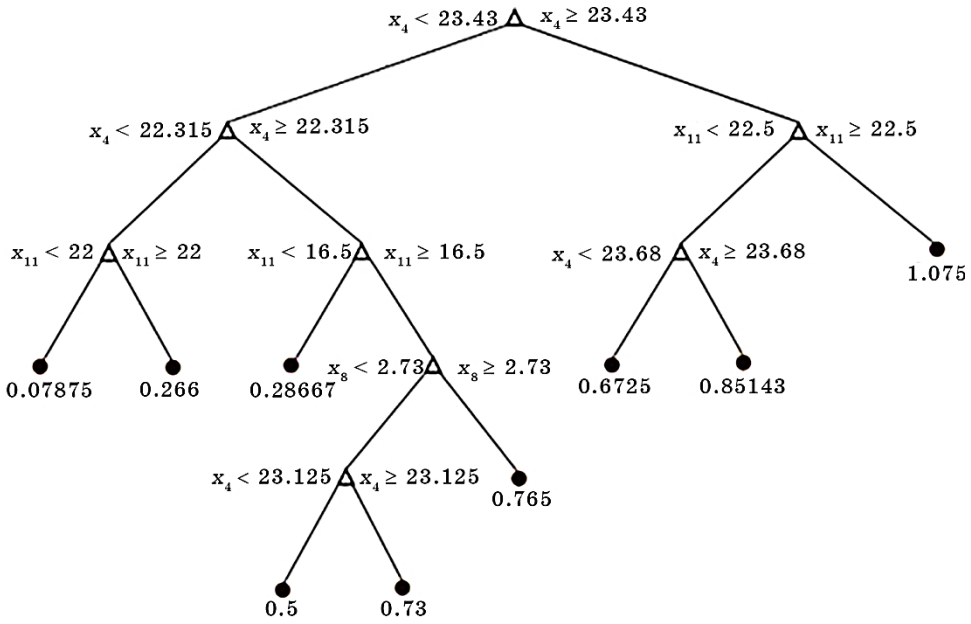



**Fig. 4.** Regression tree showing the relationship between the repassivation potential $E_{rep}$ of 06KhN28MDT alloy in a gap with a chloride-containing solution and its chemical composition and structure components.

that if $x_4(\mathrm{Cr}) < 23.43$ wt.% (item 1 of Table 4), then, it is necessary to consider the dependences when $x_4(\mathrm{Cr}) < 22.315$ wt.% and $x_{11}[d_g] < 22$ μm (items 2, 4 of Table 4). Under such conditions, the repassivation potential $E_{rep}$ of the 06KhN28MDT alloy in the gap will be 0.07875 V (item 8 of Table 4). However, if the chromium content in the studied alloy is greater than or equal to 23.43 wt.%, then it shifts intensively towards the positive side to 0.5538 V (item 1 of Table 4). This contributes to an increase in the $\Delta E$ criterion of the 06KhN28MDT alloy (see Eq. (1)) and its resistance to crevice corrosion in a chloride-containing media.

It should be noted that, as established above, the corrosion potential $E_{cor}$ of the studied alloy does not significantly shift to the positive side with an increase in its chromium content in this interval (Tables 3, 4). This trend suggests that chromium helps to reduce the intensity of general corrosion. Taking into account the intensity of chromium's influence on these potentials, we can note the positive role of chromium in the alloy resistance to crevice corrosion in a chloride-containing media. This is consistent with the information presented in Refs. [5–9, 27–31] about the effectiveness of alloying stainless steels and alloys with chromium to increase their resistance to local corrosion.

The analysis of the developed mathematical model (items 2, 5, 10 of Table 4) showed that the effect of chromium ($x_4$) on the repassivation potential $E_{rep}$ of 06KhN28MDT alloy is closely related to the mean austenite grain diameter ($x_{11}$). In particular, it was found that it is 0.336774 V, when the chromium content ($x_4$) is greater than or equal to 22.315 wt.% (item 2 of Table 4). It should be noted that under such conditions, the repassivation potential $E_{rep}$ of the studied alloy is 0.217 V more negative than when the chromium ($x_4$) content is greater than or equal to 23.43 wt.% (items 1, 2 of Table 4). This shows that even the chromium ($x_4$) content in the alloy in this interval itself significantly affects its $E_{rep}$ potential. At the same time, it was found that at such a chromium content in the alloy ($x_4 \geq 22.315$ wt.%; item 2 of Table 4), when the mean austenite grain diameter ($x_{11}$) is less than 16.5 μm (see item 5 of Table 4), its $E_{rep}$ potential is even lower and amounts to 0.286667 V (item 10 of Table 4). This proves that the grain boundaries strongly affect the potential $E_{rep}$ of the 06KhN28MDT alloy in a chloride-containing medium, shifting it to the negative side. This complicates the repassivation of local corrosion damage to the alloy in the gap with a chloride-containing media, which is associated with structural defects at the austenite grain boundaries. It should be noted that even at the maximum chromium content in the alloy under study within the production standard (Table 1), the effect of the mean austenite grain diameter on the repassivation potential $E_{rep}$ is stronger than the chromium content. This generalization is confirmed by the identified dependences between these indicators. In particular, it was recorded that

the repassivation potential $E_{rep}$ of the 06KhN28MDT alloy is 0.6725 V (item 12 of Table 4), if the mean austenite grain diameter ($x_{11}$) is less than 22.5 μm (item 3 of Table 4) and the chromium content is of 23.68 wt.% (item 6 of Table 4). At the same time, it becomes very positive (0.907895 V, item 3 of Table 3), when the mean austenite grain diameter ($x_{11}$) of the alloy under study is greater than or equal to 22.5 μm. This once again proves that defects in the alloy structure along the austenite grain boundaries have a stronger effect on its potential $E_{rep}$ in a gap with a chloride-containing medium than the ability of chromium to form passive films on the surface of local damage on it. After all, it was also found that under such conditions ($x_{11} > 22.5$ μm, item 3 of Table 4), the repassivation potential $E_{rep}$ of the 06KhN28MDT alloy is 1.075 V (item 7 of Table 4). However, even a slight decrease in the mean austenite grain diameter by 0.5 μm ($x_{11}$) > 22 μm (item 4 of Table 4) can lead to a very intense shift in the potential $E_{rep}$ of the alloy in the positive direction from 0.10266 V (item 9 of Table 4) to 0.150769 V (item 4 of Table 4). The influence of the mean austenite grain diameter ($x_{11}$) and chromium content ($x_4$) in the alloy 06HN28MDT on its $E_{rep}$ potential in a gap with a chloride-containing medium was mentioned above. At the same time, the analysis of the developed mathematical model (Fig. 4) showed that this structure indicator ($x_{11}$) of the alloy and its copper content also affect its ability to repassivate local corrosion damage in the gap. In particular, it was found that the repassivation potential $E_{rep}$ of the 06KhN28MDT alloy in the crevice is 0.471111 V (item 5 of Table 4), when its mean austenite grain diameter ($x_{11}$) is greater than or equal to 16.5 μm. At the same time, it was found that it does not significantly shift to the positive side up to 0.5 V (item 16 of Table 4), if the copper content ($x_8$) is less than 2.73 wt.% (see item 11 of Table 4) and chromium 23.125 wt.% (item 14 of Table 4). Thus, taking into account the dependence between the potential $E_{rep}$ and the content of chromium, copper, and the mean grain diameter of austenite, when it is in the range from 16.5 up to 22.5 μm, and the content of copper and chromium is less than the mentioned values, it can be noted that these indicators do not greatly affect it. At the same time, it was found that the potential $E_{rep}$ of the studied alloy varies from 0.786364 (item 6 of Table 4) to 0.851429 V (item 13 Table 4), if the chromium content ($x_4$) in it is greater than 23.68 wt.% (item 6 of Table 4) and from 0.563333 (item 11 of Table 4) to 0.765 V (item 15 of Table 4), if the copper content ($x_8$) is greater than 2.73 wt.% (item 11 of Table 4). It should be noted that at such a content of chromium and copper in the 06KhN28MDT alloy, the effect of chromium on its repassivation potential is by 1.23 times more significant than that of copper. This may be due to the fact that copper contributes to the enrichment of the passive oxide film with chromium in local corrosion damage [32].

According to the results of the analysis of dependences (item 4 of

Table 4), it was found that the repassivation potential $E_{rep}$ of the 06KhN28MDT alloy in a gap with a chloride-containing medium varies in the range from 0.523 to 0.73 V, if the chromium content in it is greater than or equal to 23.121 wt.%. At the same time, as mentioned above (items 6, 13 of Table 4), it varies in the range from 0.786364 to 0.851429 V if the chromium content is greater than 23.68 wt.%. Thus, it can be noted that the potential $E_{rep}$ of the 06KhN28MDT alloy shifts rapidly towards the positive side by 192.4 mV with an increase in its chromium content from 23.125 up to 23.68 wt.%. This leads to an increase in the alloy resistance to crevice corrosion in a chloride-containing media.

Summarizing the above, it can be noted that the repassivation potential $E_{rep}$ of the 06KhN28MDT alloy in a gap with a model chloride-containing medium depends on the content of chromium, copper, and the mean diameter of the austenite grain. It was found that it shifts to the positive side with an increase in the content of chromium and copper. The effect of chromium on the potential $E_{rep}$ of the alloy is stronger than that of copper. In addition, it is manifested by the most intense shift of the $E_{rep}$ potential in the positive direction by 192.4 mV with an increase in the chromium content from 23.121 up to 23.68 wt.%. Under such conditions, it most effectively contributes to the reparation of local corrosion damage on the alloy surface in the gap, forming dense oxide films with a minimum number of pores [33, 34], where chloride ions can adsorb from the media and contact the alloy. Copper is known [32] to contribute to the enrichment of oxide films with chromium. It was found that the potential $E_{rep}$ of the 06KhN28MDT alloy has almost the most negative value of 0.286667 V, if the mean austenite grain diameter is less than 16.5 μm. It has been found that under such conditions it shifts to the positive side to 0.765 V, if the copper content is less than 2.73 wt.%, and to 0.73 V, if the chromium content is less than 23.125 wt.%.

It has been established that the corrosion potential $E_{cor}$ of 06KhN28MDT alloy depends on the content of Cr, Mn, Ni, Cu, and the mean austenite grain diameter. In particular, it has been recorded that it has the most negative value of –0.455714 V, if the content of chromium and manganese is less than 22.215 and 0.455 wt.%, respectively. This shows that the surface of the alloy accumulates electrons due to more intense ionization of metals at the anode areas. Under such conditions, the oxide films on the alloy surface are less dense due to a decrease in its chromium content. Under such conditions, the general corrosion is accelerated, but local corrosion is 'slowed down' due to the redistribution of the anode current density between a larger numbers of anode metal dissolution places on its surface. It was found that the potential $E_{cor}$ of the alloy shifts to the positive side to –0.41 V, if the carbon content in it is less than 0.053 wt.%, *i.e.*, it is dissolved in a solid

solution of austenite. When carbides precipitate from the alloy's austenite solid solution, a slight shift of $E_{cor}$ to the negative side has been recorded. It has been found that the potential $E_{cor}$ of the alloy has the most positive value of –0.3 V, if the mean austenite grain diameter is greater than 15.5 μm. This contributes to a decrease in the $\Delta E$ criterion of the 06KhN28MDT alloy and its resistance to crevice corrosion. It was found that the potential $E_{cor}$ of the alloy significantly shifts to the negative side ($\cong$ 0.17 V), if the nickel content in it is more than 27.675 wt.%. This trend improves the alloy resistance to crevice corrosion in a chloride-containing media. This is consistent with the information in Ref. [21].

## 4. CONCLUSION

Based on the results of the analysis of mathematical models developed on the basis of regression trees, it was found that the repassivation potential $E_{rep}$ of the 06KhN28MDT alloy in the gap with a model chloride-containing medium intensively shifts to the positive side by 192.4 mV with an increase in its chromium content from 23.12 up to 23.68 wt.%. This leads to an increase in the $\Delta E$-criterion of the alloy and its resistance to crevice corrosion due to the formation of a dense chromium-containing oxide film. It has been found that the potential $E_{rep}$ of the alloy has the most negative value of 0.287 V, if the mean austenite grain diameter is less than 16.5 μm. It was found that under such conditions, the potential $E_{rep}$ of the alloy shifts to a positive value of 0.5 V if the content of copper and chromium in it is less than 2.73 and 23.125 wt.%, respectively. It is recorded that this potential shifts further in the positive direction to 0.765 and 0.73 V, if the content of copper and chromium in the alloy is more than 2.73 and 23.125 wt.%, respectively. It is shown that, under such conditions, the effect of copper on the potential $E_{rep}$ is of 0.035 V stronger than that of chromium. This is most likely due to the fact that copper contributes to the enrichment of the passive oxide film on the surface of the 06KhN28MDT alloy with chromium, which increases its resistance to crevice corrosion. It has been established that the corrosion potential $E_{cor}$ of the alloy has the most negative value of –0.4557 V, if the content of chromium and manganese in it is less than 22.215 and 0.455 wt.%, respectively. This contributes to the accumulation of electrons on the alloy surface due to the intensification of general corrosion, which leads to a decrease in the probability of crevice corrosion in a chloride-containing media. It has been shown that the precipitation of carbides (Cr, Mo) from austenite solid solution at a carbon content of more than 0.053 wt.% contributes to a slight shift of the $E_{cor}$ potential to the negative side. It is proved that the potential $E_{cor}$ of the alloy has the most positive value $\cong$ –0.38 V, if the mean austenite grain diameter is greater than 15.5

μm, regardless of the copper content. It was found that this potential shifts to the negative side by $\cong 0.17$ V, if the nickel content in the alloy is more than 27.675 wt.%. This leads to an increase in the alloy resistance to crevice corrosion.

## AUTHORS' CONTRIBUTIONS

D.A.V. carried out the experimental corrosion tests of the 06KhN28MDT alloy in model chloride-containing crevice conditions, determined the free corrosion potentials $E_{cor}$, repassivation potentials $E_{rep}$ and the $\Delta E$-criterion, participated in microstructural examinations, and prepared the initial draft of the manuscript (Introduction, Materials and Methods, Results and Discussion).

N.O.E. devised the main conceptual ideas of the study, formulated the research problem related to crevice corrosion of plate heat exchangers, designed the experimental program and test conditions, interpreted the electrochemical and corrosion behaviour of the alloy, provided a critical review of the manuscript, and supervised the scientific part of the work.

S.O.S. generated the extended dataset based on the experimental results, developed and implemented the regression-tree-based mathematical models linking $E_{cor}$, $E_{rep}$ and $\Delta E$ with the chemical composition and structural parameters of the alloy, performed the statistical analysis of model quality, and contributed substantially to the interpretation of the decision rules (Tables 3 and 4).

S.G.V. was responsible for the graphical material: performed and processed microstructural and metallographic examinations (including the characterization of titanium carbonitrides and sulphides), prepared and annotated the figures (micrographs and regression trees), and designed all tables and graphical elements illustrating the obtained results.

P.T.V. coordinated the overall project activities, including communication between the university and industrial partner, organization of access to materials and equipment, and resolution of general organizational issues; she also participated in structuring the manuscript, editing the text, and preparing the final version for submission.

All authors discussed the results, contributed to the interpretation of the findings, and approved the final version of the manuscript.

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